

PUB-NO: WO009413391A1

DOCUMENT-IDENTIFIER: WO 9413391 A1

TITLE: PROCESS FOR IMPROVING THE PERFORMANCE OF AN
ELECTROSTATIC PRECIPITATOR

PUBN-DATE: June 23, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
CHRISTIANSEN, PER B	N/A
LIN, M LINDA	N/A
HOFMANN, JOHN E	N/A
SUN, WILLIAM H	N/A
DIEP, DANIEL V	N/A

INT-CL (IPC): B01D053/36, B03C003/01

EUR-CL (EPC): B03C003/013 ; B01D053/56

US-CL-CURRENT: 423/215.5

ABSTRACT:

The present invention relates to a process for improving the performance of an electrostatic precipitator (30) through which a combustion effluent (14) is passed. The inventive process generally involves introducing urea, a urea hydrolysate or another nitrogenous composition into the effluent under conditions effective to form ammonia and produce an ammonia containing effluent; and passing the ammonia-containing effluent through an electrostatic precipitator wherein the performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.

PUB-NO: WO009413391A1

DOCUMENT-IDENTIFIER: WO 9413391 A1

TITLE: PROCESS FOR IMPROVING THE PERFORMANCE OF AN
ELECTROSTATIC PRECIPITATOR

PUBN-DATE: June 23, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
CHRISTIANSEN, PER B	N/A
LIN, M LINDA	N/A
HOFMANN, JOHN E	N/A
SUN, WILLIAM H	N/A
DIEP, DANIEL V	N/A

INT-CL (IPC): B01D053/36, B03C003/01

EUR-CL (EPC): B03C003/013 ; B01D053/56

US-CL-CURRENT: 423/215.5

ABSTRACT:

The present invention relates to a process for improving the performance of an electrostatic precipitator (30) through which a combustion effluent (14) is passed. The inventive process generally involves introducing urea, a urea hydrolysate or another nitrogenous composition into the effluent under conditions effective to form ammonia and produce an ammonia containing effluent; and passing the ammonia-containing effluent through an electrostatic precipitator wherein the performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.

PCT

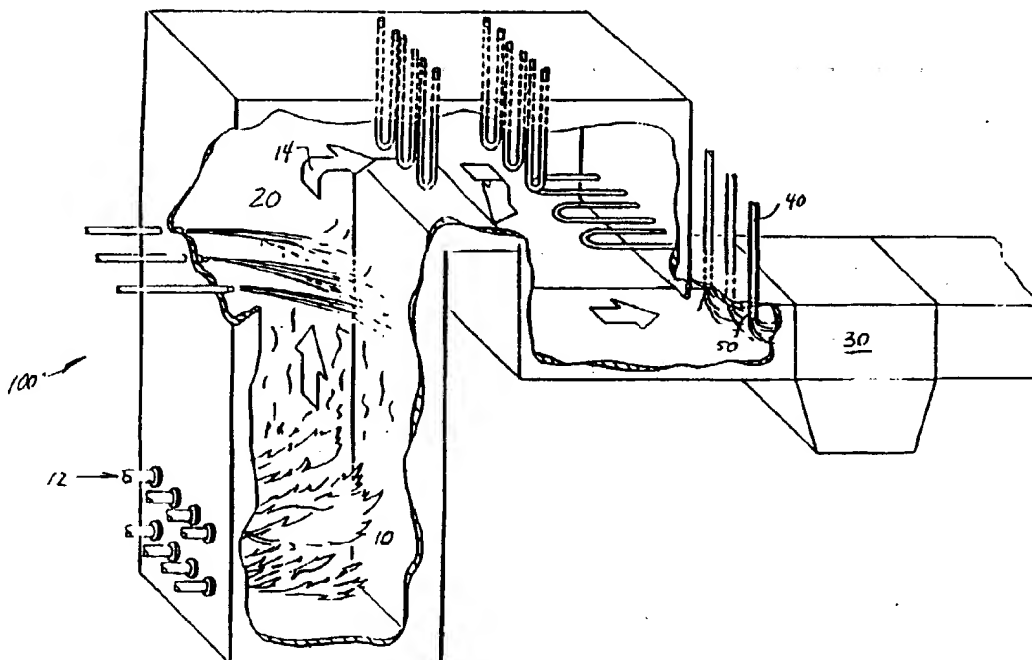
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁵ : B01D 53/36, B03C 3/01</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/13391 (43) International Publication Date: 23 June 1994 (23.06.94)</p>
<p>(21) International Application Number: PCT/US93/10843 (22) International Filing Date: 11 November 1993 (11.11.93) (30) Priority Data: 07/986,756 8 December 1992 (08.12.92) US (71) Applicant: NALCO FUEL TECH [US/US]; 1001 Frontenac Road, Naperville, IL 60563 (US). (72) Inventors: CHRISTIANSEN, Per, B.; 1192 Hobson Mill Drive, Naperville, IL 60540 (US). LIN, M., Linda; 8 South 325 Wehrli Road, Naperville, IL 60540 (US). HOFMANN, John, E.; 416 Deepwood Court, Naperville, IL 60540 (US). SUN, William, H.; 987 Amberwood Circle, Naperville, IL 60563 (US). DIEP, Daniel, V.; 1780 Margaret Lane, Aurora, IL 60505 (US). (74) Agents: CARVIS, Thaddius, J. et al.; St. Onge Steward Johnston & Reens, 986 Bedford Street, Stamford, CT 06905 (US).</p>		<p>(81) Designated States: CA, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>

(54) Title: PROCESS FOR IMPROVING THE PERFORMANCE OF AN ELECTROSTATIC PRECIPITATOR



(57) Abstract

The present invention relates to a process for improving the performance of an electrostatic precipitator (30) through which a combustion effluent (14) is passed. The inventive process generally involves introducing urea, a urea hydrolysate or another nitrogenous composition into the effluent under conditions effective to form ammonia and produce an ammonia containing effluent; and passing the ammonia-containing effluent through an electrostatic precipitator wherein the performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

DESCRIPTION

PROCESS FOR IMPROVING THE PERFORMANCE
OF AN ELECTROSTATIC PRECIPITATORRelated Applications

- 5 This application is a continuation-in-part of
copingending U.S. Patent Application entitled "Nitrogen Oxides
Reduction Using a Urea Hydrolysate", having Serial No.
07/820,907, filed in the names of von Harpe, Pachaly, Lin,
Diep, and Wegrzyn on January 16, 1992; copingending U.S.
10 Patent Application entitled "Process for the Catalytic
Reduction of Nitrogen Oxides", having Serial No.
07/879,439, filed in the names of Peter-Hoblyn, Lin, Sun,
and Hofmann on May 6, 1992; and copingending U.S. Patent
Application entitled "Highly Efficient Hybrid Process for
15 Nitrogen Oxides Reduction", having Serial No. 07/907,222,
filed in the names of Sun and Hofmann on July 1, 1992, the
disclosures of each of which are incorporated herein by
reference.

Technical Field

- 20 The present invention relates to a process and com-
position which is effective for improving the performance
of an electrostatic precipitator. The process involves the
introduction of a composition which "conditions" particu-
lates in a combustion effluent in order to facilitate
25 collection by an electrostatic precipitator.

In the combustion of carbonaceous fuels in utility boilers and other power plants, one of the results is the production of solid particulates, commonly known as fly ash. This is especially true where the fuel combusted is a solid, such as coal or municipal solid waste (MSW). The emission of these solid particulates to the atmosphere is considered undesirable and is often the subject of regulations limiting the amount which may be emitted. Accordingly, effective means for reducing the amount of particulates in a combustion effluent prior to emission to the atmosphere are widely sought.

One effective means for removing the particulates from a combustion effluent is an apparatus referred to as an "electrostatic precipitator". In an electrostatic precipitator, a combustion effluent passes between electrodes which create a corona discharge. This causes the particulates to be electrically charged. When so charged, the particulates migrate to and are deposited on a collection electrode. After exiting the electrostatic precipitator, the substantially particulate free effluent may then be emitted to the atmosphere.

One factor which has been found to be extremely important to the operation of an electrostatic precipitator is the electrical resistivity of the particulates entrained in the effluent. The resistivity of the particulates must be sufficiently high to facilitate collection. However, in many electrostatic precipitators, the resistivity of the particulates is too high, on the order of up to about 10^{13} ohm-cm or even higher. The efficiency of collection of particulates can be substantially reduced under these conditions. This

reduction in collection efficiency can severely compromise the pollution control gains provided by the electrostatic precipitator. Typically, desired resistivities range between about 10^8 and about 10^{10} ohm-cm.

5 Certain agents have been employed in order to "condition" the particulates in the effluent to maintain their electrical resistivity within desirable ranges. Included are sulfuric acid, sulfur trioxide (SO_3), and phosphoric acid, with sulfur trioxide being the most preferred and
10 most commonly used of these conditioners. In addition, another conditioner often used for improving the collection efficiency of an electrostatic precipitator is ammonia, which has also been found to improve its collection performance.

15 The exact mechanism by which ammonia conditions an effluent for electrostatic precipitation is not fully understood. However, one possible explanation is that ammonia reacts with residual sulfur trioxide in the effluent to form ammonium sulfates and bisulfates which act
20 as binders for the deposited precipitates in the electrostatic precipitator. This reduces the likelihood that deposited particulates can become re-entrained in the effluent. Another possibility is that ammonia causes particle agglomeration, which leads to more efficient
25 particle collection.

Unfortunatly, the use of ammonia as a conditioning agent for an electrostatic precipitator can be undesirable because of the toxicity and instability of ammonia. In addition, the requirement to maintain ammonia in a high
30 vapor pressure gas or liquid can also be undesirable because of the costs associated with doing so. The use of

ammonia can cause severe problems during storage, handling, and transportation, which may discourage its use as an electrostatic precipitator conditioner.

In fact, in some jurisdictions, ammonia is required to be transported and stored in the form of ammonium water, which in its most commonly utilized form is only about 25% ammonia and is sometimes as dilute as 10% ammonia. The use of ammonium water for providing ammonia to condition an electrostatic precipitator can be impractical because of the increased cost of storing and transporting such a highly dilute substance. Furthermore, the added cost of evaporating the ammonium water to evolve ammonia gas is also a disadvantageous aspect of its use.

Background Art

The conditioning of an effluent with sulfur trioxide and ammonia prior to the effluent being passed through an electrostatic precipitator has been disclosed. For instance, Rudolph and Cummings, Jr. have shown that the use of ammonia and sulfur trioxide can be very effective at improving the performance of an electrostatic precipitator, in "AmmoniaSulfur Trioxide Flue Gas Conditioning Experience at J. C. Weadock Unit #7", *Amer. Power Conf. Proc.* 49 1987, pp 58-63.

In addition, Krigmont, Coe, Jr., and Southam, in U.S. Patent 5,029,535, discuss means for controlling the addition of conditioning agents such as sulfur trioxide and ammonia to an effluent in order to optimize removal of particulate matter in an electrostatic precipitator. Likewise, Wright also discloses a system for maintaining a flow of sulfur trioxide conditioning agent into an effluent

ahead of an electrostatic precipitator by monitoring the opacity of the stack effluent in order to optimize the particulate removal process, in U.S. Patent 5,032,154.

What is desired therefore, is a process and composition for improving the operation and performance of an electrostatic precipitator by the addition of ammonia as a conditioning agent, while reducing or eliminating the need for the storage, handling, or transport of ammonia.

Disclosure of Invention

10 The present invention relates to a process for improving the performance of an electrostatic precipitator through which a combustion effluent is passed. The process involves introducing into the effluent a composition effective to form ammonia under the conditions present in the
15 effluent, especially urea or a urea hydrolysate; and passing the ammonia containing effluent through an electrostatic precipitator. The performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.

20 By the use of the process of the present invention, the performance of the electrostatic precipitator is improved by the presence of ammonia while reducing or eliminating the need for the undesirable storage, handling, and transport of ammonia or ammonium water.

25 Brief Description of the Drawings

The objects of this invention will be described and the present invention better understood and its advantages

more apparent in view of the following detailed description, especially when read with reference to the appended drawing which is a schematic illustration of a boiler utilizing the present invention.

5 Best Mode for Carrying Out the Invention

As noted above, the present invention relates to improving the performance of an electrostatic precipitator in reducing particulate levels in a combustion effluent. This is accomplished in the presence of ammonia by introducing into the effluent a treatment agent which comprises a compound or compounds which generate ammonia in the effluent. Advantageously, these compounds comprise urea or the hydrolysis products of urea. After formation of ammonia in the effluent, the effluent is then passed through an electrostatic precipitator.

In an advantageous aspect of the invention, the ammonia-generating treatment agent can be introduced into the effluent so as to reduce nitrogen oxides (NO_x , where x is an integer, generally 1 or 2) levels in the effluent, either catalytically or non-catalytically, while generating ammonia to condition the electrostatic precipitator. In this way, the most effective use of the treatment agent occurs.

The treatment agent to be introduced into the effluent comprises a non-ammonia nitrogenous composition, by which is meant a composition having at least one component which contains nitrogen as an element. The non-catalytic reduction of nitrogen oxides by such treatment agents comprises a selective, free radical-mediated process, often referred to as selective non-catalytic reduction (SNCR).

Various nitrogenous compositions, in their pure and typical commercial forms, will generate effective gas-phase NO_x reducing agents (e.g., the amidozine radical, NH[•]) when introduced in aqueous solution. Among the prominent nitrogenous compositions are urea; urea precursors; one or more of the hydrolysis products of urea (such as ammonium carbamate, ammonium carbonate, ammonium bicarbonate); other ammonium salts; and various urea complexes, including a urea hydrolysate which consists of a unique structure of ammonium carbonate and ammonium bicarbonate in a complex with ammonium carbamate; products of the reaction of urea with itself or other compositions, related compositions, or mixtures of these. Also included among these compounds are ammonium carbonate, ammonium formate, ammonium citrate, ammonium acetate, ammonium oxalate, other ammonium salts (both organic and inorganic, but particularly of organic acids), ammonium hydroxide, various stable amines, guanidine, guanidine carbonate, biguanide, guanylurea sulfate, melamine, dicyanamide, calcium cyanamide, biuret, 1,1'-azobisformamide, methylol urea, methylol urea-urea, dimethyl urea, hexamethylenetetramine (HMTA), or mixtures of the foregoing.

Enhancers are additive materials which modify the effectiveness of a pollutant-reducing agent in terms of its effective temperature window, its utilization efficiency, or the like. Among the enhancers which can be included with the treatment agent of this invention are the above materials when used in suitable combination, as well as other compositions such as hexamethylenetetramine (HMTA), oxygenated hydrocarbons such as ethylene glycol and methanol, ammonium salts of organic acids such as ammonium acetate and ammonium benzoate, heterocyclic hydrocarbons having at least one cyclic oxygen such as furfural, sugar,

molasses, 5- or 6-membered heterocyclic hydrocarbons having at least one cyclic nitrogen such as pyridine and pyrrolidine, hydroxy amino hydrocarbons such as milk or skimmed milk, amino acids, proteins and monoethanolamine and various other compounds which are disclosed as being effective at the reduction of nitrogen oxides in an effluent, or mixtures of the foregoing. Exemplary of other suitable oxygenated hydrocarbons are ketones, aldehydes, alcohols including polyols, carboxylic acids, sugars, starch hydrolysates, hydrogenated starch hydrolysates, sugar-containing residues such as molasses, and mixtures of any of these. The entire disclosures of U.S. Patents 4,719,092, 4,844,878, and 4,877,591, which describe suitable enhancers, are incorporated herein by reference.

Most preferred among the enhancers are the oxygenates, such as the oxygenated hydrocarbons, heterocyclic hydrocarbons having at least one cyclic oxygen, sugar, and molasses. In fact, several of the enhancers, especially the oxygenates and certain of the ammonium salts, can themselves function in NO_x-reducing treatment agents in an independent introduction.

The use of urea as the nitrogenous treatment agent is most common, and disclosed by Arand, Muzio, and Sotter in U.S. 4,208,386 and Arand, Muzio, and Teixeira in U.S. 4,325,924, the disclosures of each of which are incorporated herein by reference. As noted above, the use of urea or other non-ammonia nitrogenous agents (as compared to ammonia) is preferred as the nitrogenous composition of this invention since the toxicity and instability of ammonia are avoided.

The use of the hydrolysis products of urea as well as a unique urea hydrolysate for nitrogen oxides reduction has been disclosed by von Harpe and Pachaly in International Patent Application entitled "Process for the In-Line Hydrolysis of Urea", having Publication No. WO 92/02291, filed August 1, 1991; and von Harpe, Pachaly, Lin, Diep, and Wegrzyn in International Patent Application entitled "Nitrogen Oxides Reduction Using a Urea Hydrolysate", having Publication No. WO 92/02450, filed August 1, 1991, the disclosures of each of which are incorporated herein by reference.

The introduction of the hydrolysis products of urea or a urea hydrolysate as the nitrogenous composition in the treatment agent of the present invention can have significant advantages due to their ability to reduce nitrogen oxides over a relatively wide effluent temperature window, while minimizing the generation of nitrous oxide (N_2O), another pollutant.

Under the proper conditions, urea hydrolyzes to products which are believed to include ammonia (NH_3), ammonium carbamate (NH_2COONH_4) ("carbamate"), ammonium carbonate ($(NH_4)_2CO_3$) ("carbonate"), and ammonium bicarbonate (NH_4HCO_3) ("bicarbonate"). Hydrolysis generally continues sequentially from carbamate, through carbonate and then to bicarbonate, each composition being more stable than urea.

Although each of the noted hydrolysis products is individually commercially available, it is more desirable to produce them via urea hydrolysis under the conditions detailed below. This is because the thusly formed hydrolysate has advantages over the individual hydrolysis products, even if combined in the same approximate ratios. A

primary advantage is cost, since urea can be significantly less expensive than the individual hydrolysis products. Additionally, a maximum solubility of about 25% for the hydrolysate (based on initial urea concentration) has been
5 observed, which is superior to the solubility of bicarbonate, i.e., about 18%. This can be significant in terms of transportation costs and final treatment agent concentrations.

According to solubility and structural analyses,
10 including high pressure liquid chromatography (HPLC) using phosphoric acid as solvent; carbon-13 nuclear magnetic resonance spectroscopy (NMR); thermal gravimetric analysis (TGA); differential scanning calorimetry (DSC); and measurement of "P" or "M" alkalinity by acid titration, the
15 hydrolysate prepared according to this invention comprises at least in part a single unique structure of carbonate and bicarbonate which is in a complex with carbamate (expressed as carbamate·bicarbonate/carbonate). If the pressure exerted on the hydrolysate solution is sufficiently high, ammonia also produced does not flash off, but remains in solution and remains available. In addition, depending on the
20 conditions employed, residual urea may also be present.

Although a urea solution will hydrolyze under ambient conditions, typically less than 1% will do so, an insignificant amount in terms of either NO_x reduction or facilitating the collection efficiency of an electrostatic precipitator. In forming the hydrolysate, temperature, pressure, concentration of the initial urea solution, and residence time are all important parameters, and must be balanced.
30 High pressure is particularly useful because the reaction proceeds in the direction of smaller mole volumes during

the formation of carbamate and carbonate. Higher temperature and longer residence times also result in higher levels of hydrolysis. However, under equivalent pressures, temperatures, and residence times, hydrolysis decreases
5 with increases in solution concentration.

Advantageously, hydrolysis of a 10% aqueous urea solution should be conducted under pressures sufficiently high to maintain the resulting hydrolysate in solution. Such pressures will also facilitate hydrolysis. Desirably,
10 hydrolysis is performed under pressures of at least about 500 pounds per square inch (psi), more preferably at least about 650 psi. If it is desired to maintain ammonia in solution, the pressure should be at least about 750 psi. As the concentration of the initial urea solution is in-
15 creased, the pressure is preferably increased to achieve equivalent results.

There is no true upper limit of pressure in terms of facilitating hydrolysis; rather, any upper limits comprise practical as opposed to technical limits, since higher
20 pressures, i.e., pressures above about 3000 psi, require vessels able to stand such pressures, which are generally more expensive and usually unnecessary.

At the desired pressures, the temperatures and residence times can be varied. Temperatures of only about
25 250°F will ensure the presence of some hydrolysate (e.g., no more than about 5%), whereas temperatures of about 600°F to 700°F will ensure that virtually all the urea has been converted to hydrolysate. Residence times can vary between about three minutes and about 15 minutes, preferably about
30 five minutes to about 10 minutes. It will be recognized that the upper temperature and residence time limits are

less important since exceeding them will not result in lower levels of hydrolysis or a less effective hydrolysate, it is believed.

The temperature and residence time for urea hydrolysis are related, and one (i.e., time) can be decreased as the other (i.e., temperature) is increased. For instance, hydrolysis at 400°F for 10 minutes may be generally equivalent to hydrolysis at 500°F for five minutes and hydrolysis at 600°F for three minutes.

As noted, hydrolysis proceeds to consecutively form carbamate, carbonate, and bicarbonate. Although all three are present even under the least severe conditions, it is desired that the ratio of carbamate to bicarbonate/carbonate in the hydrolysate be about 10:1 to about 1:200, more preferably about 2:1 to about 1:100 for greatest effectiveness. This can be achieved by hydrolyzing at a fluid temperature of at least about 325°F for about five minutes or longer.

Most preferably, the hydrolysis of urea is conducted in the presence of metal catalysts such as copper catalysts like copper nitrate, nickel catalysts like nickel sulfate, and iron catalysts like iron (III) nitrate, with the copper and nickel catalysts preferred. Since such catalysts enhance urea hydrolysis, greater hydrolysis levels can be achieved with equivalent hydrolysis conditions by the use of the catalysts. The catalyst metal is mixed into the urea solution prior to hydrolysis. For instance between about five and about 15, preferably about 10 parts per million (ppm) of catalyst (as metal) is mixed into a 10% urea solution, whereas about 20 to about 60 ppm, preferably about 50 ppm is mixed into a 25% urea solution.

In order to effectively supply sufficient urea hydrolysate to reduce nitrogen oxides and condition the effluent for feeding through an electrostatic precipitator, it is desired that at least about 25% of the urea be hydro-
5 lyzed. More preferably, at least about 60% of the urea is hydrolyzed, most preferably at least about 80%.

The level of hydrolysis achieved under any particular set of conditions can easily be determined, for instance, by measuring the "P" and "M" alkalinity of the hydrolyzed
10 solution. For example, a 10% solution of urea has a pH of 7.3 with 0 "P" alkalinity and 0.002% "M" alkalinity as CaCO_3 . When hydrolyzed, the hydrolysate has a pH of about 9.5, with up to 9% "P" alkalinity and 20.2% "M" alkalinity. By comparing the alkalinity of a hydrolyzed solution with a
15 theoretical maximum, using the fresh urea solution as a reference, the level of hydrolysis can be estimated.

Hydrolysis level can also be determined using conductivity in the same manner as alkalinity can be used. The conductivity of a 10% urea solution is about 1.2 milli-
20 mhos, whereas a 10% urea solution which has been completely hydrolyzed has a conductivity of about 120 milli-mhos.

The urea hydrolysis reaction is advantageously carried out "on site" (by which is meant within convenient transport distance, such as about 50 miles, of the combustion
25 source to be treated), and, most advantageously, in-line because of the economy, stability, and relative safety of urea for transport and storage. Further, the solubility of the hydrolysate is lower than that of urea, making urea more practical to transport.

When the inventive hydrolysate is formed in-line, as discussed hereinbelow, the urea solution should comprise sufficient urea to provide the desired level of hydrolysate. Advantageously, the urea solution comprises up to
5 about 50% urea by weight, more preferably about 5% to about 45% urea by weight. Most preferably, the solution comprises about 10% to about 25% urea by weight.

For efficiency, though, it may be desirable to hydrolyze a more concentrated urea solution, i.e., about 45%
10 to about 60% by weight, to minimize the heat requirements during hydrolysis. This can most advantageously be done when hydrolysis is performed "on site", that is, at or near the location of the boiler in which the hydrolysis products are to be introduced, but not in-line. The hydrolyzed
15 solution can then be diluted to the appropriate level. On-site urea hydrolysis can be performed in a suitable vessel in which the urea solution can be raised to the desired pressures and temperatures.

As noted, hydrolysis of urea can be performed in-line,
20 that is, while the urea solution is being supplied to an injector or other introduction means to be introduced into a combustion effluent. This can be accomplished by passing the aqueous solution of urea through a supply conduit (referred to as a reaction conduit or tube) and applying
25 heat and pressure.

The conduit can be any of the conventional tubes or pipes currently used to supply urea, ammonia, or other solutions to a combustion effluent for NOx reductions, or ammonia solutions as a conditioner for an electrostatic
30 precipitator or in operative connection therewith, provided the conduit length and flow rates are sufficient to provide

the desired residence times, as would be understood by the skilled artisan. Thus the process can be practiced without significantly effecting the efficiency of current conditioning processes since it does not require substantial
5 alteration or retrofitting of current installations.

In fact, heat for the hydrolysis reaction can be provided by the effluent itself. As would be understood by the skilled artisan, a conventional heat exchanger can be installed which transfers the desired amount of heat from
10 the effluent to the conduit through which the urea solution is flowing, in order to avoid the need for an independent heat source.

As noted, the heat exchanger for heating the urea solution to perform hydrolysis may be positioned in the
15 effluent stream and, as a result of this, the heat required for facilitating the urea hydrolysis reaction is withdrawn from the effluent to avoid the need for an independent heat source. Such heat exchanger preferably forms a unit together with the apparatus on which the injector or other
20 injection means are arranged within the effluent stream. The heat exchanger at the same time cools the injector means such as the injection lances, which is desirable at high effluent temperatures.

The heat exchanger is preferably constructed in the
25 form of a jacket around the injection lance. The heated and hydrolyzed urea solution is passed from the heat exchanger directly into the combustion effluent or to a flash drum positioned outside the effluent, and the gaseous or liquid phase formed is separately supplied to the injec-
30 tors of the injection lance, while pressurized air may optionally be added to the gaseous phase.

The above-described compounds can be introduced according to processes which maximize the nitrogen oxides reductions achieved while controlling or minimizing the production of other pollutants. Such processes are described in, for instance, U.S. 4,777,024 to Epperly, Peter-Hoblyn, Shulof, Jr., and Sullivan; U.S. 5,057,293 to Epperly, Peter-Hoblyn, Shulof, Jr., Sullivan, Sprague, and O'Leary; U.S. 4,780,289 to Epperly, O'Leary, and Sullivan; and U.S. 5,017,347 to Epperly, Sullivan, Sprague, and O'Leary, the disclosures of each of which are incorporated herein by reference.

The urea, urea hydrolysate, or other nitrogenous composition can be introduced into the effluent by suitable introduction means under conditions effective to reduce NOx and form ammonia in order to condition particulates to improve the performance of an electrostatic precipitator. Suitable introduction means include injectors, such as those disclosed by Burton in U.S. Patent 4,842,834, or DeVita in U.S. Patent 4,915,036, the disclosures of each of which are incorporated herein by reference. One especially preferred type of injection means is an injection lance, especially a lance of the type disclosed by Peter-Hoblyn and Grimard in International Publication No. WO 91/00134, filed July 4, 1989, entitled "Lance-Type Injection Apparatus", the disclosure of which is incorporated herein by reference.

When the treatment agent comprises urea, a urea hydrolysate, or another nitrogenous treatment agent, without a non-nitrogenous hydrocarbon component, it is preferably introduced at an effluent temperature of about 1500°F to about 2100°F, more preferably about 1700°F to about 2100°F. In fact, depending on parameters such as concentration and

droplet size, effective nitrogen oxides reductions can be achieved using urea or a urea hydrolysate at temperatures above 2100°F. When the treatment agent also comprises one of the enhancers discussed above, it can be introduced at
5 an effluent temperature of about 1200°F to about 1750°F, more preferably about 1350°F to about 1750°F or higher.

These effluent temperatures at the point of introduction can be varied depending on the amount of ammonia desired in the effluent to condition the electrostatic
10 precipitator, particular components of the compound, and other effluent conditions, such as the effluent oxygen level. In fact, the use of an enhancer will generally reduce the level of ammonia in the effluent. If the enhancer reduces the ammonia level to below that desired for
15 electrostatic precipitator conditioning, the enhancer can be introduced at a lower level, or not at all, so that sufficient ammonia is present.

The compound is introduced into the effluent at a molar ratio of the nitrogen in the compound to the baseline
20 nitrogen oxides level in the effluent of about 1:10 to about 10:1. More preferably, the molar ratio of compound nitrogen to baseline NO_x level is about 1:5 to about 5:1 (in the situation where enhancers are introduced without a nitrogenous component, they are introduced at a weight
25 ratio of about 1:10 to about 10:1, preferably about 1:5 to about 5:1). By "baseline nitrogen oxides level" is meant the level (measured or calculated) of nitrogen oxides in the effluent prior to introduction of the compound.

The baseline NO_x level is also used in calculating the
30 percentage of nitrogen oxides reduced by measuring the level of nitrogen oxides in the effluent after treatment,

dividing that number by the baseline nitrogen oxides level, subtracting from unity and multiplying by 100 to give the NOx reduction expressed as percentage of baseline.

The treatment agent is preferably supplied to the
5 effluent as a solution, most preferably an aqueous solution, and its concentration in the solution will be at least effective to reduce the level of NOx in the effluent. The solution can be varied from saturated to very dilute. At higher effluent temperatures, the concentration of
10 nitrogenous compound will be more dilute, say less than about 20% at about 2000°F, and from about 0.5% to about 10% at these or higher temperatures. On the other hand, concentrations of from about 20% to about 40% are more typical for temperatures below about 2000°F.

15 Advantageously, the size of the droplets of solution will be within the range of from about 10 to about 10,000, and preferably greater than about 50 microns. The droplet size is important to enable uniform mixing of the treatment agent with the effluent and penetration of the treatment
20 agent sufficiently along the internal boiler path that it can achieve its intended function. The size of the droplets will preferably be increased with increasing temperature. At temperatures below about 2000°F, droplet sizes of less than about 150 microns are quite effective, while at
25 higher temperatures the droplets should be larger, and preferably larger than about 500 microns.

The presence of sufficient ammonia can, at least partially, be ensured by varying the effluent temperature at which the nitrogenous treatment agent is introduced (by,
30 for instance, adjusting the location at which the introduction occurs), specific composition and introduction ratio

of the treatment agent. These parameters should be adjusted to provide the desired amount of ammonia in the effluent. This can be accomplished using the process and techniques described in U.S. 4,780,289, U.S. 4,830,839, and/or
5 U.S. 5,017,347, the disclosures of each of which are incorporated herein by reference, which utilize the nitrogen oxides reduction versus effluent temperature curve of a treatment regimen and its curve plateau to control the presence of secondary pollutants such as ammonia while
10 reducing NOx.

By "nitrogen oxides reduction versus effluent temperature curve" is meant a plot of the data points generated when a treatment regimen is effected by introducing a treatment agent into an effluent over a range of effluent
15 temperatures and the nitrogen oxides reduction at each introduction temperature is measured (and usually expressed in terms of percent baseline). "Curve plateau" refers to that region of a nitrogen oxides reduction versus effluent temperature curve where the NOx reduction is substantially
20 maximized over a range of temperatures and preferably encompasses at least two data points (of course a skilled artisan will recognize that a curve plateau will not necessarily be flat due to "data scatter" and other practical data generation effects). By "treatment regimen" is meant
25 to the introduction (such as by injection) of a treatment agent into an effluent and the conditions under which the treatment agent is introduced, such as treatment agent components (by which is meant the ingredients or chemical formulation of the treatment agent), treatment agent dilu-
30 tion (by which is meant the concentration of treatment agent components when the treatment agent used comprises a solution), relative presence of treatment agent components (by which is meant the relative weight ratio or fractions

of the components which form the chemical formulation which makes up the treatment agent), etc.

The introduction temperature of a treatment agent, especially a nitrogenous treatment agent, has predictable effects on both nitrogen oxides reductions achieved and on the amount of ammonia remaining in the effluent after introduction of the treatment agent. With knowledge of this information, the nature (i.e., composition) and introduction of the treatment agent can be carefully coordinated to produce the desired amount of ammonia in the effluent even where the choice of introduction temperatures cannot be altered (in many boilers, retrofitting or providing access for different injection levels is not always possible or economically feasible). Typically, this involves introducing a treatment agent such that it is acting on the "left" side of the plateau of its nitrogen oxides reduction versus effluent temperature curve at the effluent temperature at the point of introduction, in order to generate ammonia for conditioning of the particulates.

The introduction or other equivalent parameters such as the normalized stoichiometric ratio can also be adjusted to provide ammonia (by normalized stoichiometric ratio is meant the ratio of the concentration of theoretically available reducing-radicals such as NH_2 or NCO radicals to the concentration of nitrogen oxides in the effluent; alternatively, the molar ratio of the treatment agent to the NO_x concentration can be used in place of NSR when the chemistry of reduction is not well defined; the term NSR as used herein will also be understood to encompass molar ratio when appropriate).

These methods all cause operation to occur at a different location on the curve and can be achieved in one of two ways. First, the position on the curve at which the treatment regimen being used is being effected can be translated by effecting the treatment regimen at a lower effluent temperature. It will readily be observed that effecting the treatment regimen at a lower effluent temperature will translate the position of operation on the curve further to the left.

Effecting the treatment regimen at a different effluent temperature can be accomplished by performing the treatment agent introduction at a location where the effluent temperature is different from the original introduction location. However, this method for effecting the treatment regimen at a different effluent temperature can oftentimes be impractical because access to the boiler interior is often limited to specific points, due to various possible physical restrictions, etc. Introduction at a location where the effluent temperature is at a desired level, therefore, is often not possible.

Altering the operating load of the boiler (i.e., fuel supply rate) will also cause a change in effluent temperature and can, theoretically at least, be used to alter effluent temperature at the treatment agent introduction location by changing operating load. In practice, though, altering the boiler operating load is not preferred because the effluent condition is altered in more ways than the temperature parameter. Nitrogen oxides level, as well as other parameters such as carbon monoxide level, are altered along with effluent temperature. Furthermore, the boiler operating load is usually maintained at a certain level to

produce a specific, required output and is not available as a factor which can be altered in this manner.

A second method for operating at a different location on the curve is to vary one or more of the parameters of the treatment regimen being effected. For instance, the varied parameter can be the specific components of the treatment agent, the dilution of the treatment agent when in solution with a concomitant variation in treatment agent introduction rate to maintain the NSR of the treatment regimen, the relative presence of treatment agent components, or combinations of any of the above. By varying treatment regimen parameters, the original nitrogen oxides reduction versus effluent temperature curve is replaced by the nitrogen oxides reduction versus effluent temperature curve for the varied treatment regimen. Selection of the parameter(s) to be varied and in what way they are varied can replace the original curve with a curve which is "shifted" to the right, thereby leading to operation on the shifted curve at a different position.

For example, if the treatment regimen being effected comprises a treatment agent which is an aqueous solution of 10% urea hydrolysate and 15% furfural, and the effluent temperature at the treatment location is 175°F, thereby operating toward the right side of the treatment regimen nitrogen oxides reduction versus effluent temperature curve plateau, then varying the treatment regimen by varying the treatment agent components by eliminating the furfural replaces the original curve with a curve at which introduction at that effluent temperature operates further towards the left side of the curve plateau. Likewise, if the treatment regimen being effected comprises a treatment agent which is an aqueous solution of 10% urea hydrolysate

- and 15% furfural, and the effluent temperature at the point of introduction is 1665°F, thereby operating near the midpoint of the treatment regimen nitrogen oxides reduction versus effluent temperature curve plateau, then varying the
- 5 treatment regimen to vary the treatment agent to replace the 15% furfural with 15% ethylene glycol replaces the original curve with a curve at which introduction at that effluent temperature operates further towards the right side of the curve plateau.
- 10 Of course, the two methods for operating at different points on the curve plateau disclosed according to the present invention are not mutually exclusive, but can in fact be combined. In other words, the effluent temperature can be varied along with one or more treatment regimen
- 15 parameters.

In an alternate embodiment of this invention, the nitrogenous compounds discussed above are introduced into the effluent at an effluent temperature wherein they readily convert to ammonia in order to facilitate the catalytic

20 reduction of nitrogen oxides (referred to as selective catalytic reduction, or SCR), provided sufficient ammonia remains to condition the electrostatic precipitator. The effluent temperature at the point of introduction should also be chosen so as to avoid the utilization of the com-

25 pound or the ammonia generated therefrom, to reduce NO_x via an SNCR pathway. Although some utilization in this manner is not disadvantageous, there is the possibility of some by-product formation (such as carbon monoxide and nitrous oxide) which could become undesirable emissions themselves.

- 30 Accordingly, introduction of the urea, urea hydrolysate, or other nitrogenous compound (such as by the means

discussed above) should be at an effluent temperature below about 1500°F, preferably below about 1350°F. More preferably, the effluent temperature is between about 230°F and about 1200°F. When there is a substantial amount of urea present (i.e., when urea itself is being introduced or when there is less than about 80% hydrolysis), the effluent temperature should be at least about 350°F. Most preferably, the effluent temperature at the point of introduction of the treatment agent should be between about 550°F and about 950°F.

When the treatment agent comprises a urea hydrolysate, it may be at ambient temperature prior to introduction or, alternatively, it may be at or above its boiling point. In this way, the hydrolysate can flash off immediately upon introduction into the effluent, which might provide advantages in minimizing air requirements for atomization, etc.

After introduction of the urea, urea hydrolysate, or other composition, the treated effluent, which now contains ammonia, is passed over a catalyst. The catalyst used is one capable of reducing the effluent nitrogen oxides concentration in the presence of ammonia. Such a catalyst comprises, for instance, activated carbon, charcoal or coke, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, copper oxide, manganese oxide, chromium oxide, noble metals such as platinum group metals like platinum, palladium, rhodium, and iridium, or mixtures of these. Other catalyst materials conventional in the art and familiar to the skilled artisan can also be utilized. These catalyst materials are typically mounted on a support such as a ceramic substance or a zeolite although other art known supports can also be used.

The ammonia-containing effluent is most preferably passed over the catalyst while the effluent is at a temperature between about 230°F to about 950°F. In this manner, the ammonia present in the effluent by the introduction of the hydrolyzed urea solution most effectively facilitates the catalytic reduction of nitrogen oxides.

Additionally, the two above-described embodiments can be combined. In this way, the nitrogenous treatment agent is introduced so as to reduce nitrogen oxides via an SNCR pathway, wherein sufficient ammonia is created to facilitate the catalytic reduction of NO_x, and then to condition the electrostatic precipitator.

Moreover, the nitrogenous compound can be introduced independent of either an SNCR or SCR pathway. In this case, the urea, hydrolyzed urea, or other compound (preferably in solution, especially aqueous solution) of this invention is introduced into the effluent at an effluent temperature wherein the compound readily converts to ammonia in order to condition the electrostatic precipitator, under conditions substantially identical to those described above, except no SNCR or SCR NO_x reduction occurs prior to the electrostatic precipitator.

Advantageously, the nitrogenous treatment agent is introduced into the effluent in an amount sufficient to provide a volume level of the ammonia generated in the effluent (whether after SNCR, SCR, or introduction of the compound without SNCR or SCR) sufficient to lower the resistivity of the particulates to below about 10^{13} ohm-cm, more preferably below about 10^{10} ohm-cm. Generally, the volume level of ammonia should be at least about 3.0 parts per million (ppm). More preferably, the treatment agent is

introduced into the effluent to provide a level of ammonia of about 3.0 ppm to about 100 ppm, most preferably about 10.0 ppm to about 50.0 ppm.

In addition to the nitrogenous compound introduced to condition the electrostatic precipitator with ammonia, it is also desirable to introduce a sulfur oxide, especially SO_3 , as a conditioner for the electrostatic precipitator. The sulfur compound is advantageously introduced into the effluent at a level of at least about 6.1 ppm, more preferably about 6.5 to about 10.2 ppm. In fact, it has been found that there is a synergy between SO_3 and ammonia in conditioning an electrostatic precipitator -- the performance increase from the introduction of both is greater than the sum of either alone.

After introduction of the treatment agent (and, optionally, SO_3), the treated effluent, which now contains ammonia, is passed through an electrostatic precipitator. The particular design and operational characteristics of suitable electrostatic precipitators are familiar to the skilled artisan. In fact, virtually any design suggested to date can be utilized.

The effluent is preferably passed through the electrostatic precipitator while the effluent is at a temperature between about 70°F and about 1350°F, more preferably between about 250°F and about 850°F. In some experimental electrostatic precipitators, the operational temperature can be as high as about 1500°F. In this manner, the ammonia present in the effluent by the introduction of the treatment agent most effectively facilitates the precipitation of particulates.

In a typical installation of the present invention as illustrated in the attached figure, a boiler 100 comprises a flame zone 10 wherein a fuel 12 is combusted to form an effluent 14. Effluent 14 travels from flame zone 10
5 through effluent conduit 20. An electrostatic precipitator 30 is disposed in effluent conduit 20 such that effluent 14 passes therethrough while at a temperature of 300°F.

An apparatus for the in-line hydrolysis of urea 40 as discussed above is disposed at effluent conduit 20 such
10 that injection means 50 extends into effluent 14 at a point where the temperature of effluent 14 is 700°F. A 25% aqueous solution of urea is passed through apparatus 40 and the resulting urea hydrolysis products injected into effluent 14 through injection means 50, where they degrade to
15 ammonia. The ammonia travels to electrostatic precipitator 30 which causes precipitation of particulates present in the effluent in the presence of the thusly produced ammonia.

Use of the present invention reduces or eliminates the
20 requirement for the transport, storage and handling of large amounts of ammonia or ammonium water. Even where the inventive process does not provide all of the ammonia required for conditioning of the effluent to facilitate electrostatic precipitator performance, the reduction of
25 the amount needed still provides significant advantages in terms of both safety and cost.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention and it is not intended to detail all of
30 those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the de-

scription. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the following claims.

What is claimed is:

1. A process for improving the performance of an electrostatic precipitator, comprising:
 - a) treating urea under conditions effective to form a urea hydrolysate;
 - 5 b) introducing said urea hydrolysate into an effluent from the combustion of a carbonaceous fuel under conditions effective to form ammonia and produce an ammonia-containing effluent; and
 - c) passing the ammonia-containing effluent through
- 10 an electrostatic precipitator, wherein the performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.
2. The process of claim 1, wherein said urea hydrolysate is formed by subjecting an aqueous solution of urea to heat and pressure for a time sufficient to at least partially hydrolyze said urea to form a hydrolysate comprising a
- 5 complex of ammonium carbamate with ammonium bicarbonate/ammonium carbonate, where the ratio of ammonium carbamate to ammonium bicarbonate/ammonium carbonate is about 10:1 to about 1:200.
3. The process of claim 2, wherein said pressure is at least about 500 psi.
4. The process of claim 3, wherein said aqueous urea solution is heated to at least 300°F for from about three minutes to about 14 minutes to at least partially hydrolyze said urea.
5. The process of claim 2, wherein the urea solution is contacted with a catalyst for the hydrolysis of urea.

6. The process of claim 5, wherein said urea hydrolysis catalyst is selected from the group consisting of metals, metal oxides, metal salts, and mixtures thereof.

7. The process of claim 1, wherein said urea hydrolysate is introduced into the effluent at a level sufficient to provide a volume level of ammonia effective to maintain particulate resistivity at less than about 10^{13} ohm-cm.

8. The process of claim 7, wherein said urea hydrolysate is introduced into the effluent in an amount sufficient to provide at least about 3.0 parts per million of ammonia.

9. The process of claim 1, wherein said urea hydrolysate is formed at the site of the electrostatic precipitator.

10. The process of claim 9, wherein said urea hydrolysate is formed in-line as it is being fed into the combustion effluent.

11. The process of claim 1, which further comprises introducing sulfur trioxide into the effluent as a conditioner for the electrostatic precipitator.

12. The process of claim 11, wherein sulfur trioxide is introduced into the effluent in an amount of at least about 6.1 parts per million.

13. A process for improving the performance of an electrostatic precipitator, comprising:

- a) introducing a nitrogenous composition into an effluent from the combustion of a carbonaceous fuel under conditions effective to form ammonia and produce an ammonia-containing effluent; and

b) passing the ammonia-containing effluent through an electrostatic precipitator, wherein the performance of the electrostatic precipitator is improved by the presence of ammonia in the effluent.

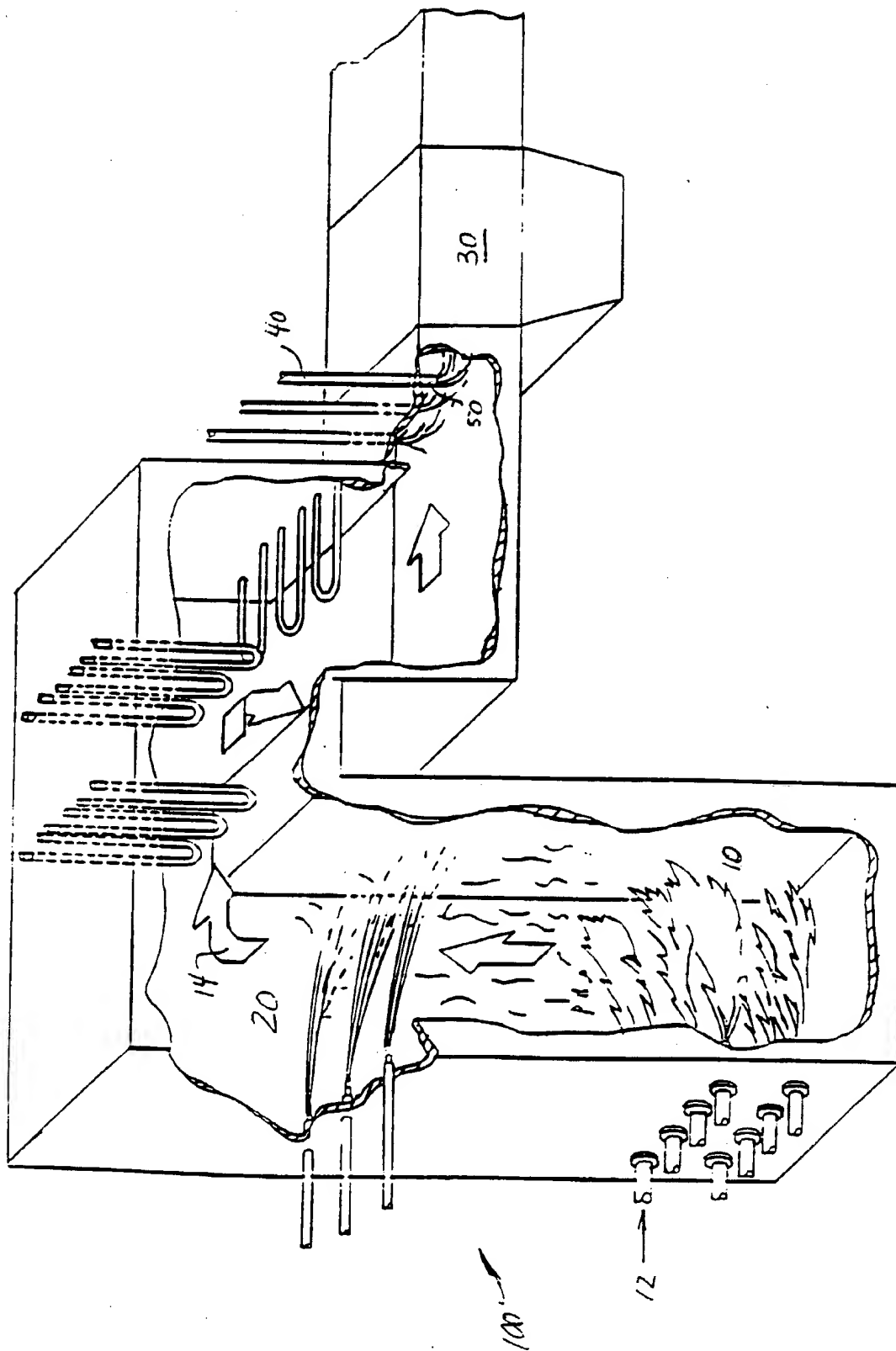
14. The process of claim 13, wherein said nitrogenous composition comprises urea, a urea hydrolysate, or mixtures thereof.

15. The process of claim 13, wherein composition is introduced into the effluent at a level sufficient to provide a volume level of ammonia effective to maintain particulate resistivity at less than about 10^{13} ohm-cm.

16. The process of claim 15, wherein composition is introduced into the effluent in an amount sufficient to provide at least about 3.0 parts per million of ammonia.

17. The process of claim 13, which further comprises introducing sulfur trioxide into the effluent as a conditioner for the electrostatic precipitator.

18. The process of claim 17, wherein sulfur trioxide is introduced into the effluent in an amount of at least about 6.1 parts per million.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10843

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : B01D 53/36; B03C 3/01

US CL : 423/235; 55/5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/235; 55/5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,070,162 (KOBER ET AL.) 24 January 1978, Col. 4, Lines 27-54, C ol3, Lines 34-48.	1-18
Y	SU, A, 589-023 (Ferr Metal EFFL Purif) 17 January 1978, See the translated abstract.	1-4
Y	JP, A, 2-191528 (BABCOCK HITACHI K.K.) 27 July 1990 See the translated abstract.	1-10,13-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

13 January 1994

Date of mailing of the international search report

MAR 17 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

TOM DUNN

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-2533